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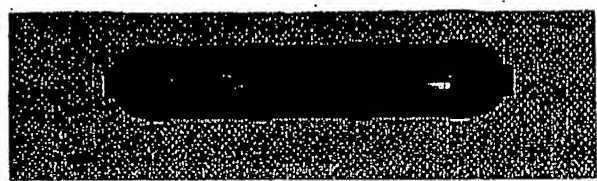
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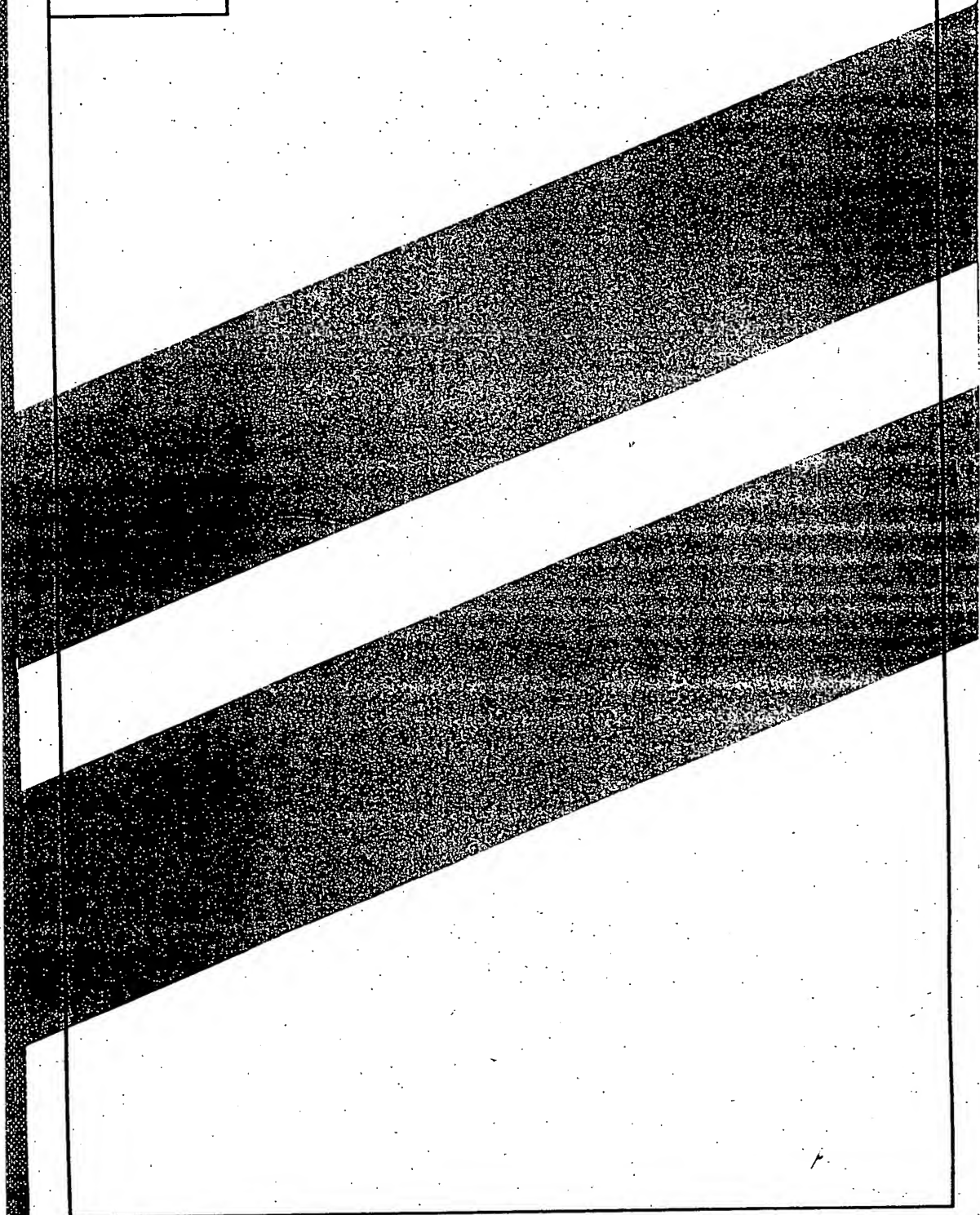
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60/160,510

PROVISIONAL
APPLICATION
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9-16-78



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PATENT APPLICATION



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CONTENTS

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1.	Application	1
2.	Specification	1
3.	Claims	1
4.	Abstract	1
5.		
6.		
7.		
8.		
9.		
10.		
11.		
12.		
13.		
14.		
15.		
16.		
17.		
18.		
19.		
20.		
21.		
22.		
23.		
24.		
25.		
26.		
27.		
28.		
29.		
30.		
31.		
32.		

**METHOD OF REMOVING ORGANIC LIXIVIAN FROM
COPPER SX-EW ELECTROLYTE STREAM"**

The present invention relates generally to leaching systems and specifically to treatment systems for removing an organic lixiviant from a leaching solution.

THE PROBLEM

5 The present invention generally relates to the removal of copper ions from copper ore, and more particularly to enhanced removal of copper ions using a microfiltration or ultrafiltration process which removes entrained organic materials and suspended solid and colloidal materials from
10 the aqueous electrolyte solution before or after it enters the electrowin tankhouse. This process improves the copper hydrometallurgical mining process through more efficient copper electrowinning.

15 The techniques used to remove copper from raw ore determine the overall efficiency of the copper mining operation. Hydrometallurgical copper mining operations using a leaching system and a copper extraction plant, such as a solvent extraction/electrowinning (SX/EW) plant, are now accepted processes in the copper mining industry.
20 Currently, electrowon copper accounts for about 30% of total U.S. copper production. Worldwide, there are more than 26 major heap, dump, or in-situ leaching operations using SX/EW, with a total capacity of ~800,000 tons of copper

annually. The industry trend continues towards this technology as higher-grade ores are depleted and smelting costs increase. Other advantages of this technology, such as the ability to process low-grade ores, low labor requirements, ease of operation in remote areas, and low operating costs, make it attractive to mining companies.

"Copper hydrometallurgy", in which copper ions are leached or otherwise extracted from raw ore using liquid chemical agents, has been of interest since as early as the 17th century when copper recovery methods involving iron precipitating agents from sulfuric acid based copper solutions were tested. The hydrometallurgical circuit consists of copper leaching and copper recovery.

First, a copper leaching agent, "lixiviant", is selected for use in leaching copper ions from copper ore. Representative lixiviants include but are not limited to sulfuric acid (H_2SO_4), a combination of H_2SO_4 and ferric sulfate, $Fe_2(SO_4)_3$ (primarily for sulfide containing ore materials), acidic chloride solutions (e.g. ferric chloride, $FeCl_3$) or cupric chloride, $CuCl_2$, nitrate solutions, ammonia, and ammonium salt compositions. Sulfuric acid is by far the most common lixiviant. The lixiviant is applied to the ore (which is stacked or piled in a large heap or dump) via a sprinkler type system and allowed to percolate downwardly into the ore. As a result, copper ions are leached from the ore and collected within the lixiviant to generate a

lixiviant product that consists of a copper ion concentration (also known as a "pregnant leach solution"). The lixiviant exits the bottom of the ore and is collected. Further information regarding the lixiviant leaching process is disclosed in U.S. Patent No. 5,476,591 to Green et al., which is incorporated herein by reference.

Next, a copper recovery process is used to selectively extract copper from the collected lixiviant. Representative copper recovery processes include but are not limited to solvent extraction/electrowin (SX/EW), direct electrowinning, ion exchange-electrowin (IX/EW), and iron precipitation. Solvent extraction/electrowin is presently the most common copper recovery process. SX/EW technology was implemented in the 1960s with the development of special organic extractants for copper. The SX/EW process consists of three closed solution loops. In the first loop, the acid leach solution containing valuable copper ions and a multitude of other metal ions is fed into a mixer/settler tank where it is contacted with a copper-extracting organic liquid, commonly referred to as "lix". The "lix" preferentially extracts from 70 to 90% of the copper ions from the acid leaching feed solution. The second closed loop extraction step involves contacting the loaded organic with an electrolyte stream from the electrowinning process. The copper ions are transferred from the organic solution or "lix" to the lean electrolyte. In the third and final

closed loop, the rich electrolyte flows between a cathode plate and an insoluble anode, where 70-90% of the copper is removed through "plating". The electrochemical cell "plates" a stainless steel electrode with copper using an applied current. The copper plated cathode plates are then periodically removed from the process to obtain the solid, high purity copper product.

The copper electrowinning "EW" process must be improved to overcome inherent problems such low current efficiency, poor copper product quality, and poor copper removal from the stainless steel cathode electrode. The present invention specifically provides an improved method for copper recovery in which the entrained organic in the electrolyte is removed with a membrane system, leaving an organic - free electrolyte for superior copper electrowinning. The direct result of organic removal with the membrane process is better copper product quality. Accordingly, the invention represents an advance in the art of copper mining technology, as described in detail herein.

SUMMARY OF THE INVENTION

These and other needs are met by the process of the present invention which recovers a metal from a metal-containing material. The process includes the steps of:

5 (a) contacting a metal leaching agent with the metal-containing material to solubilize the metal in a pregnant leach solution;

(b) contacting the pregnant leach solution with an organic collector to transfer at least a portion of the solubilized metal to the organic collector to form a pregnant organic solution including a metal-containing organic collector and a stripped pregnant leach solution, wherein the stripped pregnant leach solution may contain at least a portion of the organic collector;

10 (c) contacting the pregnant organic solution with an electrolyte solution to form a stripped pregnant organic solution comprising most of the organic collector and a pregnant electrolyte solution comprising at least most of the metal and some of the organic collector;

15 (d) filtering at least one of the pregnant electrolyte and a second electrolyte solution formed from the pregnant electrolyte solution with a filter (either before or after the electrowinning process) to form a concentrate containing at least most of the organic collector and a permeate. The permeate is preferably substantially free of organic materials and suspended solid and colloidal materials.

5 The process can further include the steps of recycling
the concentrate to steps (b) or (c). As set forth in U.S.
Provisional Application, "Method of Removing Organic
Lixiviant from Copper SX/EW Raffinate Stream," having
Attorney File No. 3376-18PROV, filed October 30, 1997, which
is incorporated herein by this reference, the stripped
pregnant leach solution can also be filtered to recover the
organic collector.

10 By recovering the organic collector in the concentrate,
the process can reduce, or eliminate, organic collector in
the electrowinning tankhouse and can recover the organic
collector from the concentrate for reuse. The substantial
absence of residual organic collector from the
electrowinning tankhouse addresses many inherent problems in
15 copper electrowinning, including low current efficiency,
poor copper product quality, and poor copper removal from
the stainless steel cathode electrode. Accordingly, the
process provides a large, direct economic benefit.

20 The metal, organic collector, and leaching agent can be
a variety of materials. The metal is preferably selected
from the group consisting of copper, cobalt, gold, silver,
uranium, nickel and mixtures thereof. The organic collector
is preferably selected from the group consisting of
hydroxyphenyl oximes (aka the reagents sold under the trade
25 names "LIX-622N," "LIX-54," "LIX 63," "ACORGA P-5100," "ACORGA
M5640" and "ALAMINE 336" (uranium extraction)) and mixtures

thereof. The leaching agent is preferably selected from the group consisting of sulfuric acid, a chloride, a nitrate, ammonia, ammonium salts, a sulfate, a cyanide, a thiocyanate and mixtures thereof.

5 The filter is preferably a micro- or ultrafilter. The filter preferably has a pore size ranging from about 30Å (or 0.003 microns) to about 1000Å (or .01 microns) and more preferably ranging from about 50Å (or .05 microns) to about 1,000Å (0.1 microns).

10 The filtration step preferably causes the concentrate to constitute less of the electrolyte solution than the permeate. More preferably, the concentrate constitutes no more than about 50% and most preferably no more than about 5% of the electrolyte solution. More preferably, the
15 permeate constitutes at least about 50% and most preferably at least about 95% of the electrolyte solution.

 The permeate comprises at least most of the electrolyte in the electrolyte solution. Preferably, the permeate comprises at least about 50% and more preferably at least
20 about 95% of the electrolyte in the electrolyte solution.

 The concentrate comprises at least most of the organic collector in the electrolyte solution. Preferably, the concentrate comprises at least about 95% and more preferably at least about 99% of the organic collector in the
25 electrolyte solution. Further details concerning the filtration step and the filter are set forth in U.S. Patents

5,476,591; 5,310,486, and 5,116,511, each of which is incorporated fully herein by reference.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a flow schematic of an embodiment of a process according to the present invention; and

Fig. 2 is a flow schematic of another process embodiment according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The process improvements claimed in the present invention will result from utilizing a microfiltration or ultrafiltration membrane system to process the electrolyte before or after it enters the electrowin tankhouse.

As illustrated by Figure 1, a strong sulfuric acid solution 4 passes downwardly through a heap or dump 8 of low-grade copper ore and a liquid product 12 is produced which contains remaining amounts of acid in combination with metal ions. In a first loop 16, the liquid product 12 containing copper ions and other dissolved metals is fed to a mixer/settler tank 20 where it is contacted with organic material (e.g., a lix). The organic material forms compounds with the copper ions. The mixture forms two phases--an organic phase and an inorganic phase. The organic phase is removed to form the organic solvent 24. The inorganic phase is removed to form the acid leach

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solution 28. In a second loop 32, the organic solvent 24 is contacted in a mixer/settler tank 36 with an electrolyte stream 40 from the electrowinning circuit. The copper ions are transferred from the organic solvent 24 to the electrolyte stream 40. The resulting mixture forms two phases--a copper lean organic solvent 44 and a copper rich electrolyte 48. The two phases are separated with the organic solvent 44 being recycled to the mixer/settler tank 20 and the copper rich electrolyte 48 being further treated for copper recovery. In a third and final closed loop 52, the copper rich electrolyte 48 exiting the mixer/settler tank 36 is passed through a microfiltration or ultrafiltration membrane system 56. The membrane system 56 separates the rich electrolyte into two streams: permeate 60 and concentrate 64. The concentrate 64 consists of substantially all the entrained organic in the electrolyte 48. The permeate 60 consists of a substantially organic-free solution X to be sent directly to the electrowon tankhouse 68. In the electrowon tankhouse 68, the permeate or organic-free solution 60 flows between a cathode plate and an insoluble anode, where copper is removed through "plating". The electrochemical cell "plates" a stainless steel electrode with copper using an applied current. The copper plated cathode plates are then periodically removed from the process to obtain the solid, high-purity copper product.

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The membrane system 56 would process 100 - 10,000 gallons per minute of rich electrolyte, with 40-95% of the feed flow becoming permeate product (organic - free). Typical microfiltration and ultrafiltration membranes used would be MQW, G, J, K, DS-7 and Q series elements from Osmonics/Desal of Vista, CA. These spiral wound elements use poly acrylonitril, PTFE (Teflon), PVDF, polyarimid and/or polysulfone membrane materials. The described membranes span the microfiltration/ultrafiltration membrane category, with molecular weight cut-offs of 3,000 to 200,000 MWCO and pore sizes of 0.003 microns to 0. 1 micron.

A typical system would process 1,000 gpm of electrolyte through 348 each 8 inch spiral wound JX membrane elements. The system would split the feed flow into 900 gpm of permeate 60 and 100 gpm of concentrate.

What is claimed is:

1. A process for recovering a metal from a metal-containing material, comprising:

(a) contacting a metal leaching agent with the metal-containing material to solubilize the metal in a pregnant leach solution;

(b) contacting the pregnant leach solution with an organic collector to transfer at least a portion of the solubilized metal to the organic collector to form a pregnant organic solution including a metal-containing organic collector and a stripped pregnant leach solution;

(c) contacting the pregnant organic solution with an electrolyte solution to form a stripped pregnant organic solution comprising most of the organic collector and a pregnant electrolyte solution comprising at least most of the metal and some of the organic collector;

(d) filtering at least one of the pregnant electrolyte solution and a second electrolyte solution formed from the pregnant electrolyte solution with a filter to form a concentrate containing at least most of the organic collector and a permeate.

2. The process of Claim 1, further comprising:

recycling the concentrate to at least one of steps (b) and (c).

3. The process of Claim 1, further comprising:
(e) recovering the organic collector from the concentrate.

4. The process of Claim 1, wherein the metal is selected from the group consisting of copper, gold, silver, uranium, nickel and mixtures thereof.

5. The process of Claim 1, wherein the organic collector is selected from the group consisting of hydroxyphenyl oximes, alamines, and mixtures thereof.

6. The process of Claim 1, wherein the leaching agent is selected from the group consisting of sulfuric acid, a chloride, a nitrate, ammonia, ammonium salts, a sulfate, a cyanide, a thiocyanate, and mixtures thereof.

7. The process of Claim 1, wherein the filter has a pore size ranging from about 0.003 to about 0.1 microns.

8. The process of Claim 1, wherein the concentrate constitutes no more than about 50% of the at least one of the pregnant electrolyte solution and the second electrolyte solution.

9. The process of Claim 1, wherein the permeate constitutes at least about 50% of the at least one of the pregnant electrolyte solution and the second electrolyte solution.

10. The process of Claim 1, wherein the permeate comprises at least most of the electrolyte in the at least one of the pregnant electrolyte solution and the second electrolyte solution.

11. The process of Claim 1, wherein the permeate comprises at least about 50% of the electrolyte in the at least one of the pregnant electrolyte solution and the second electrolyte solution.

12. The process of Claim 1, wherein the concentrate comprises at least about 95% of the organic collector in the at least one of the pregnant electrolyte solution and the second electrolyte solution.

13. The process of Claim 1, wherein the stripped pregnant leach solution contains at least a portion of the organic collector and further comprising:

filtering the stripped pregnant leach solution with a second filter to form a second concentrate containing at least most of the organic collector and a second permeate.

14. The process of Claim 13, further comprising:
contacting the second permeate with metal-containing
material.

15. A process for recovering a metal from a metal-
containing material, comprising:

(a) contacting a pregnant metal-containing
solution with an organic collector to transfer at least a
5 portion of a solubilized metal in the pregnant metal-
containing solution to the organic collector to form a
pregnant organic solution including a metal-containing
organic collector and a stripped solution;

(b) contacting the pregnant organic solution with
10 an electrolyte solution to form a stripped pregnant organic
solution comprising most of the organic collector and a
pregnant electrolyte solution comprising at least most of
the copper and some of the organic collector;

(c) filtering at least one of the pregnant
15 electrolyte solution and a second electrolyte solution
formed from the pregnant electrolyte solution with a filter
to form a concentrate containing at least most of the
organic collector and a permeate; and

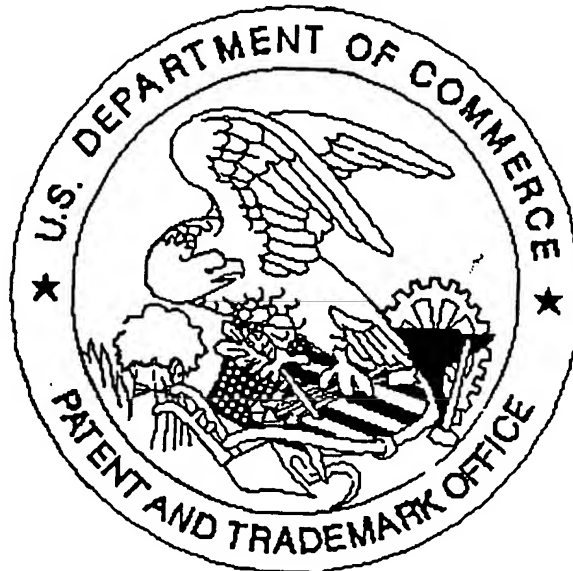
(d) recovering the metal from the at least a
20 portion of the pregnant electrolyte solution.

ABSTRACT

A treatment system for removing organic lixiviant from a copper electrolyte solution. An aqueous copper electrolyte stream containing entrained organic, i.e. "electrolyte" from a copper extraction process, is passed
5 through a microfiltration or ultrafiltration membrane system to produce an organic rich concentrate and an organic free permeate. In one embodiment, the permeate is fed directly to the copper electrowin tankhouse for recovery of superior grade cathode copper. In another embodiment, the permeate is
10 returned to the mixer tank for reuse. In either embodiment, The concentrate is returned to the mixer tank where the copper rich organic solvent and aqueous copper lean electrolyte are combined. The result of this membrane
15 filtration of the copper electrolyte is removal of organic previously passed on to the electrowin tankhouse. The organic in the rich electrolyte results in decreased current efficiency, decreased copper cathode quality, difficulty in removing the copper sheet from the stainless steel cathode, and a safety concern with the explosion potential of the
20 organic.

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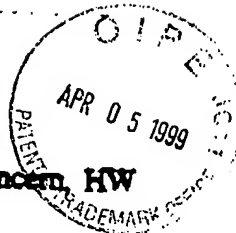


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VERIFIED STATEMENT (DECLARATION) CLAIMING ALL ENTITY STATUS
(37 CFR 1.9(f) and 1.27(c)) - SMALL BUSINESS CONCERN



I hereby declare that I am an official empowered to act on behalf of the small business concern, **HW PROCESS TECHNOLOGIES, INC.** of 1208 Quail Street, Lakewood, Colorado 80215.

I hereby declare that the above-identified small business concern qualifies as a small business concern as defined in 13 CFR 121.3-18, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees under section 41(a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention, entitled "METHOD OF REMOVING ORGANIC LIXIVANT FROM COPPER SX-EW ELECTROLYTE STREAM" and identified as Attorney File No. 3376-21PROV3.

If the rights held by the above-identified small business concern are not exclusive, each individual, concern or organization having rights to the invention is listed below* and no rights to the invention are held by any person, other than the inventor, who could not qualify as a small business concern under 37 CFR 1.9(c) or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

*NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

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I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

Date: 3-31-99

By: [Signature]

Dennis Green
Vice-President

REQUEST FOR ACCESS OF ABANDONED APPLICATION UNDER 37 CFR 1.14(a)

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I hereby request access under 37 CFR 1.14(a)(3)(iv) to the application file record of the above-identified ABANDONED application, which is: (CHECK ONE)

- ☒ (A) referred to in United States Patent Number 6156186 column _____
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United States Patent [19]
Mueller et al.



US006156186A

[11] Patent Number: 6,156,186
[45] Date of Patent: *Dec. 5, 2000

[54] METHOD FOR REMOVING
CONTAMINANTS FROM PROCESS
STREAMS IN METAL RECOVERY
PROCESSES

[75] Inventors: Jeff Mueller, Boulder; Dennis H.
Green, Arvada, both of Colo.

[73] Assignee: HW Process Technologies, Inc.,
Lakewood, Colo.

[*] Notice: This patent is subject to a terminal dis-
claimer.

[21] Appl. No.: 09/183,683

[22] Filed: Oct. 30, 1998

Related U.S. Application Data

[60] Provisional application No. 60/100,510, Sep. 16, 1998,
provisional application No. 60/100,494, Sep. 16, 1998,
provisional application No. 60/077,878, Mar. 13, 1998,
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sional application No. 60/064,279, Oct. 30, 1997, provi-
sional application No. 60/099,717, Sep. 10, 1998, and
provisional application No. 60/100,497, Sep. 16, 1998.

[51] Int. Cl.⁷ C25C 1/00; C25C 1/16;
C25C 1/20; C15G 1/12; B01D 11/00

[52] U.S. Cl. 205/560; 205/568; 205/569;
205/570; 205/571; 205/581; 205/582; 205/605;
205/606; 210/650

[58] Field of Search 205/560, 568,
205/571, 580, 589, 594, 569, 570, 581,
582, 590, 591, 605, 606; 210/650

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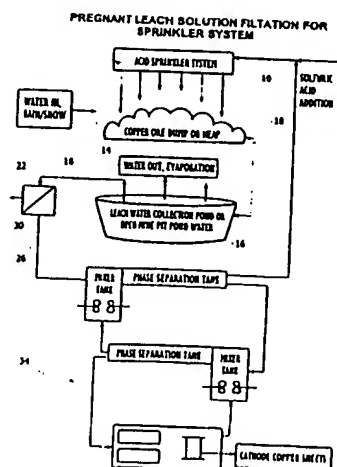
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Primary Examiner—Donald R. Valentine
Attorney, Agent, or Firm—Sheridan Ross P.C.

[57] ABSTRACT

The present invention is directed to a process for removing
various contaminants (e.g., organic collectors, contaminant
metals or spectator ions, and/or suspended and colloidal
solids) from process streams in leaching processes. The
contaminant removal is performed by one or more mem-
brane filtration systems (e.g., nanofilters, ultrafilters, and/or
microfilters) treating process streams including, the pregnant
leaching solution, the barren raffinate, and the lean and rich
electrolytes.

33 Claims, 7 Drawing Sheets



PATENT APPLICATION SERIAL NO. _____

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PROVISONAL APPLICATION COVER SHEET

request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c)(2).

Docket Number

3376-13PROV2

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TITLE OF THE INVENTION (280 characters max)

"A TREATMENT SYSTEM FOR PRODUCING CLEAN SULFURIC ACID SOLUTION FROM COPPER ELECTROLYTE
SOLUTION FOR REGENERATION OF COPPER SELECTIVE ION EXCHANGE RESIN"

CORRESPONDENCE ADDRESS

Douglas W. Swartz, Esq.
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1700 Lincoln Street, Suite 3500
Denver

STATE	Colorado	ZIP CODE	80203	COUNTRY	United States of America
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ENCLOSED APPLICATION PARTS (check all that apply)

X	Specification	Number of Pages	13	X	Small Entity Statement	
X	Drawing(s)	Number of Sheets	1	X	Other (specify)	Recordation of Assignment and Assignment

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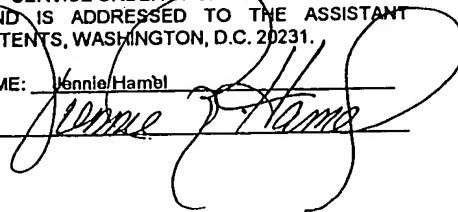
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VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS
(37 CFR 1.9(f) and 1.27(c)) - SMALL BUSINESS CONCERN

I hereby declare that I am an official empowered to act on behalf of the small business concern, HW PROCESS TECHNOLOGIES, INC. of 1201 Quail Street, Lakewood, Colorado 80215.

I hereby declare that the above-identified small business concern qualifies as a small business concern as defined in 13 CFR 121.3-18, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees under section 41(a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention, entitled "A TREATMENT SYSTEM FOR PRODUCING CLEAN SULFURIC ACID SOLUTION FROM COPPER ELECTROLYTE SOLUTION FOR REGENERATION OF COPPER SELECTIVE ION EXCHANGE RESIN" and identified as Attorney File No. 3376-13PROV, described in the specification filed herewith.

If the rights held by the above-identified small business concern are not exclusive, each individual, concern or organization having rights to the invention is listed below* and no rights to the invention are held by any person, other than the inventor, who could not qualify as a small business concern under 37 CFR 1.9(c) or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

*NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

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I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

Date: 11/19/97

By: Harold E. Whatley

Harold E. Whatley

Vice President Finance and Administration

1201 Quail Street

Lakewood, Colorado 80215

A TREATMENT SYSTEM FOR PRODUCING CLEAN
SULFURIC ACID SOLUTION FROM COPPER ELECTROLYTE SOLUTION
FOR REGENERATION OF A COPPER SELECTIVE ION EXCHANGE RESIN

FIELD OF THE INVENTION

5 The present invention generally relates to the removal of copper and metal ions from copper electrolyte solution, providing a superior acid stripping and/or rinsing solution for removal of copper from a copper selective ion exchange resin.

10 THE PROBLEM

15 The techniques used to remove copper from raw ore determine the overall efficiency of the copper mining operation. Hydrometallurgical copper mining operations using a leaching system and a copper extraction plant, such as an ion exchange/electrowinning (IX/EW) plant, are now accepted processes in the copper mining industry. Currently, electrowon copper accounts for about 30% of total U.S. copper production. The industry trend continues towards hydrometallurgical technology as higher-grade ores are
20 depleted and smelting costs increase. Other advantages of hydrometallurgical technology, such as the ability to process low-grade ores, low labor requirements, ease of operation in remote areas, and low operating costs, make it attractive to

mining companies.

"Copper hydrometallurgy," in which copper ions are leached or otherwise extracted from raw ore using liquid chemical agents, has been of interest since as early as the 17th century when copper recovery methods involving iron precipitating agents from sulfuric acid based copper solutions were tested. The hydrometallurgical circuit consists of copper leaching and copper recovery.

First, a copper leaching agent, "lixiviant," is selected for use in leaching copper ions from copper ore. Representative lixiviants include but are not limited to sulfuric acid (H_2SO_4), a combination of H_2SO_4 and ferric sulfate ($Fe_2(SO_4)_3$) (primarily for sulfide containing ore materials), acidic chloride solutions (e.g. ferric chloride, $FeCl_3$) or cupric chloride, $CuCl_2$), nitrite solutions, ammonia, and ammonium salt compositions. Sulfuric acid is by far the most common lixiviant. The lixiviant is applied to the ore (which is stacked or piled in a large heap or dump) via a sprinkler type system and allowed to percolate downwardly into the ore. As a result, copper ions are leached from the ore and collected within the lixiviant to generate a lixiviant product that consists of a copper ion concentration (also

known as "pregnant leach solution"). The lixiviant exits the bottom of the ore and is collected.

Next, a copper recovery process is used to selectively extract copper from the collected lixiviant. Representative copper recovery processes include but are not limited to solvent extraction/electrowin (SX/EW), direct electrowinning, ion exchange--electrowin (IX/EW), and iron precipitation. Solvent extraction/electrowin is presently the most common copper recovery process. Typical copper production costs using SX/EW are ~\$0.70 per pound of copper. A more recent copper recovery technology, IX/EW technology, is of interest because of its ability to produce copper for less than \$0.50 per pound of copper produced. The IX/EW process consists of a continuous or non-continuous ion exchange process using a copper specific ion exchange resin such as DOW XFX-43084 chelating resin. Acid leach solution ("pregnant leach solution") containing valuable copper ions and a multitude of other metal ions is fed into resin columns. Here, the copper ions are selectively loaded onto the resin by adsorption, exchanging copper ions for hydrogen ions. When the resin is loaded with copper ions, solution exiting the electrowinning system or "lean electrolyte" (containing 25-100 grams of

5 sulfuric acid) is used to strip the copper from the resin by exchanging hydrogen ions for copper ions. The copper "rich electrolyte" then flows between a cathode plate and an insoluble anode, where 70-90% of the copper is removed through "plating." The electrochemical cell "plates" a stainless steel electrode with copper using an applied current. The copper plated cathode plates are then periodically removed from the process to obtain the solid, high purity copper product.

10 The IX/EW copper recovery process must be improved to overcome inherent problems such as poor stripping of the ion exchange resin and availability of metal-free, acidic rinse water. For example, the copper selective ion exchange resin is currently stripped using lean electrolyte from the copper
15 electrowinning process. However, the "lean electrolyte" still contains about 25-100 grams of copper. This copper content in the lean electrolyte results in incomplete stripping of the copper from the ion exchange resin. This is because the concentration driving force between the copper on the resin
20 and the copper in the lean electrolyte solution is not as great as the driving force between the copper on the resin and a solution containing little or no copper ions.

SUMMARY OF THE INVENTION

It is an objective of the present invention to provide an improved method for recovery of valuable metals using an ion exchange resin. More particularly, it is an objective to
5 provide an improved method for stripping copper from an ion exchange resin.

These and other objectives are addressed by the method of the present invention. The method for recovering a valuable metal from a solution containing the valuable metal, includes
10 the steps of:

(a) contacting a pregnant solution containing the valuable metal with an ion exchange resin to absorb the valuable metal onto the ion exchange resin;

(b) passing an ion exchange stripping solution through a
15 membrane to remove solubilized valuable metal ions and form a treated stripping solution and a concentrate containing the solubilized valuable metal ions; and

(c) contacting the treated stripping solution with the ion exchange resin to strip the valuable metal from the ion
20 exchange resin. The valuable metal is preferably selected from the group consisting of copper, nickel, cobalt, gold, silver, uranium and mixtures thereof, with copper being most

preferred. The method provides for relatively high removal rates of valuable metals from the ion exchange resin using the treated stripping solution. This is so because the concentration driving force for the valuable metals on the resin to be solubilized by the treated stripping solution is relatively aggressive due to the absence of metal ions from the treated stripping solution.

The pregnant solution can be the product of a number of processes, such as leaching. In leaching processes, a material containing the valuable metal is contacted with a lixiviant to form the pregnant solution. The lixiviant solubilizes the valuable metal and thereby forms the pregnant solution.

In one configuration, the stripping solution is a raffinate solution from an electrowinning circuit. The stripping solution commonly contains a leaching agent, such as an acid, and dissolved ions of the valuable metal. In some cases, the stripping solution can contain about 10 g/l or more of the dissolved ions of the valuable metal.

The passing step (b) is preferably performed using a nanofiltration membrane. Preferred nanofiltration membranes have a pore size ranging from about 5Å to about 100Å, more

preferably from about 7Å to about 50Å, and most preferably from about 8Å to about 20Å.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 depicts an embodiment of a leaching process
5 according to the present invention.

DETAILED DESCRIPTION OF THE DRAWINGS

The process of the present invention specifically provides an improved IX/EW copper recovery process in which the lean electrolyte is separated into a copper-free, more
10 aggressive ion exchange stripping solution (purer sulfuric acid/water solution) for enhanced stripping of copper, and a concentrated copper-rich electrolyte for direct electrowinning. Accordingly, the invention represents an advance in the art of copper mining technology, as described
15 in detail herein. This process improves the IX/EW copper recovery process through more efficient copper stripping from the ion exchange resin, and higher copper concentrations for electrowinning.

An embodiment of the present invention is shown in Figure
20 1. The process improvements depicted in Figure 1 result from utilizing an ultrafiltration or nanofiltration membrane system to process the lean electrolyte exiting from the

electrowinning plant. As described above and shown in Figure 1, the lixiviant 10, a dilute sulfuric acid solution, is applied to the top of the heap or dump 14, a pregnant leach solution 18 containing copper ions ("pregnant leach solution") is collected from the bottom of the ore heap or dump 14 and passed through a series of ion exchange columns 22 containing a copper selective ion exchange resin. When the ion exchange resin is contacted with the pregnant leach solution, the resin selectively loads copper ions by exchanging hydrogen ions for copper ions and forms a depleted solution 26 which may or may not be combined with additional sulfuric acid to form the lixiviant 10.

At the end of the copper loading cycle, the ion exchange resin is stripped of copper ions by contacting the resin with the treated stripping solution 30, from the electrowinning circuit 34. Hydrogen ions from the concentrated sulfuric acid treated stripping solution (permeate) are exchanged for copper ions, resulting in a copper "rich electrolyte" solution 38 that reports to the electrowinning circuit 34 for copper recovery. The regenerated column is rinsed with additional treated electrolyte (acidic water) to remove remaining copper. Then, the column is placed back in the pregnant leach solution

circuit to load copper ions again.

In the improved process, the "lean electrolyte" 42 is processed through an ultrafiltration or nanofiltration membrane system 46. The membrane system 46 separates the lean electrolyte into two streams: the treated stripping solution 30 and concentrate 50. The concentrate 50 consists of the majority of the copper ions present in the lean electrolyte. The treated stripping solution 30 consists of a minority of the copper ions, or very few of the copper ions in the lean electrolyte. However, the sulfuric acid is not separated by the ultrafiltration or nanofiltration membranes, and it remains equally in the concentrate and treated stripping solution streams.

The treated stripping solution 30 is used for the stripping and rinsing steps of the ion exchange resin. The clean, high acidity permeate solution provides a superior solution for these process steps. The high copper, high acidity concentrate stream is returned to the electrowinning circuit for copper recovery.

The membrane system in the invention would process a bleed stream of lean electrolyte from the electrowinning circuit tank house. The system would process 10-1,000 gallons

per minute of electrolyte, with about 35-75% of the feed flow becoming permeate product. Typical ultrafiltration membranes used would be G series elements from Osmonics/Desalination Systems of Vista, CA, and typical nanofiltration membranes
5 used would be DK series elements from Osmonics/Desalination Systems of Vista, CA. Further information regarding the nanofiltration membrane process is disclosed in U.S. Patent Nos. 5,476,591 and 5,310,486 to Green et al., which are incorporated herein by reference. A typical system would
10 process 500 gpm of electrolyte through 201 each 8-inch spiral wound DK membrane elements. The system would split the feed flow into 250 gpm of permeate and 250 gpm of concentrate, with about 90% rejection of the copper ions into the concentrate stream.

What is claimed is:

1. A method for recovering a valuable metal from a solution containing the valuable metal, comprising:

(a) contacting a pregnant solution containing the valuable metal with an ion exchange resin to absorb the valuable metal onto the ion exchange resin;

(b) passing a stripping solution through a membrane to remove solubilized valuable metal ions and form a treated stripping solution and a concentrate containing the solubilized valuable metal ions; and

(c) contacting the treated stripping solution with the ion exchange resin to strip the valuable metal from the ion exchange resin.

2. The method of Claim 1, wherein the valuable metal is selected from the group consisting of copper, nickel, cobalt, gold, silver, uranium, and mixtures thereof.

3. The method of Claim 1, further comprising:
contacting a material containing the valuable metal with a lixiviant to form the pregnant solution.

4. The method of Claim 1, wherein the stripping solution is a raffinate solution from an electrowinning

circuit.

5. The method of Claim 1, wherein the stripping solution comprises at least about 10 g/l of the valuable metal.

6. The method of Claim 1, wherein in the passing step (b) the membrane has a pore size ranging from about 5Å to about 100Å.

7. The method of Claim 1, wherein in the passing step (b) the concentrate comprises at least 50% of the solubilized valuable metal ions in the stripping solution.

ABSTRACT

A treatment system for removing copper ions from a copper electrolyte solution. The copper containing solution, i.e., 'electrolyte' from a copper electrowinning process, is passed
5 through an ultrafiltration or nanofiltration membrane system to produce a copper-ion rich concentrate and a relatively copper-ion free permeate. The copper ion free permeate is used to strip copper ions from a copper ion exchange resin. The copper-rich concentrate is returned to the head of the
10 copper electrowinning process for copper recovery. The membrane filtration of the copper electrolyte results in enhanced copper ion exchange resin stripping, and higher copper concentrations for electrowinning.

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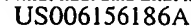
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(II) Patent Number: 6,156,186

[45] **Date of Patent:** *Dec. 5, 2000

- ## OTHER PUBLICATIONS

"Cross Contamination of ODC Solvent Extraction Circuits"; *Society for Mining, Metallurgy, and Exploration, Inc.*; Preprint No. 96-162; Mar. 11-14, 1996; pps. 1-10.

Primary Examiner—Donald R. Valentine
Attorney, Agent, or Firm—Sheridan Ross P.C.

The present invention is directed to a process for removing various contaminants (e.g., organic collectors, contaminant metals or spectator ions, and/or suspended and colloidal solids) from process streams in leaching processes. The contaminant removal is performed by one or more membrane filtration systems (e.g., nanofilters, ultrafilters, and/or microfilters) treating process streams including, the pregnant leaching solution, the barren raffinate, and the lean and rich electrolytes.

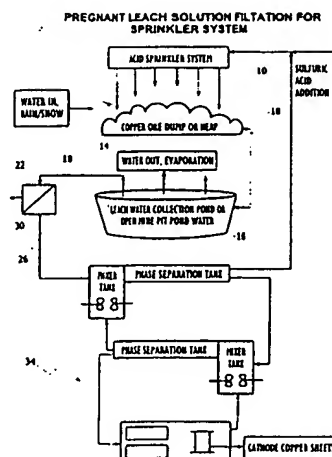
Related U.S. Application Data

- U.S. PATENT DOCUMENTS

- (List continued on next page.)

FOREIGN PATENT DOCUMENTS

- WO 94/27711 12/1994 WIPO.



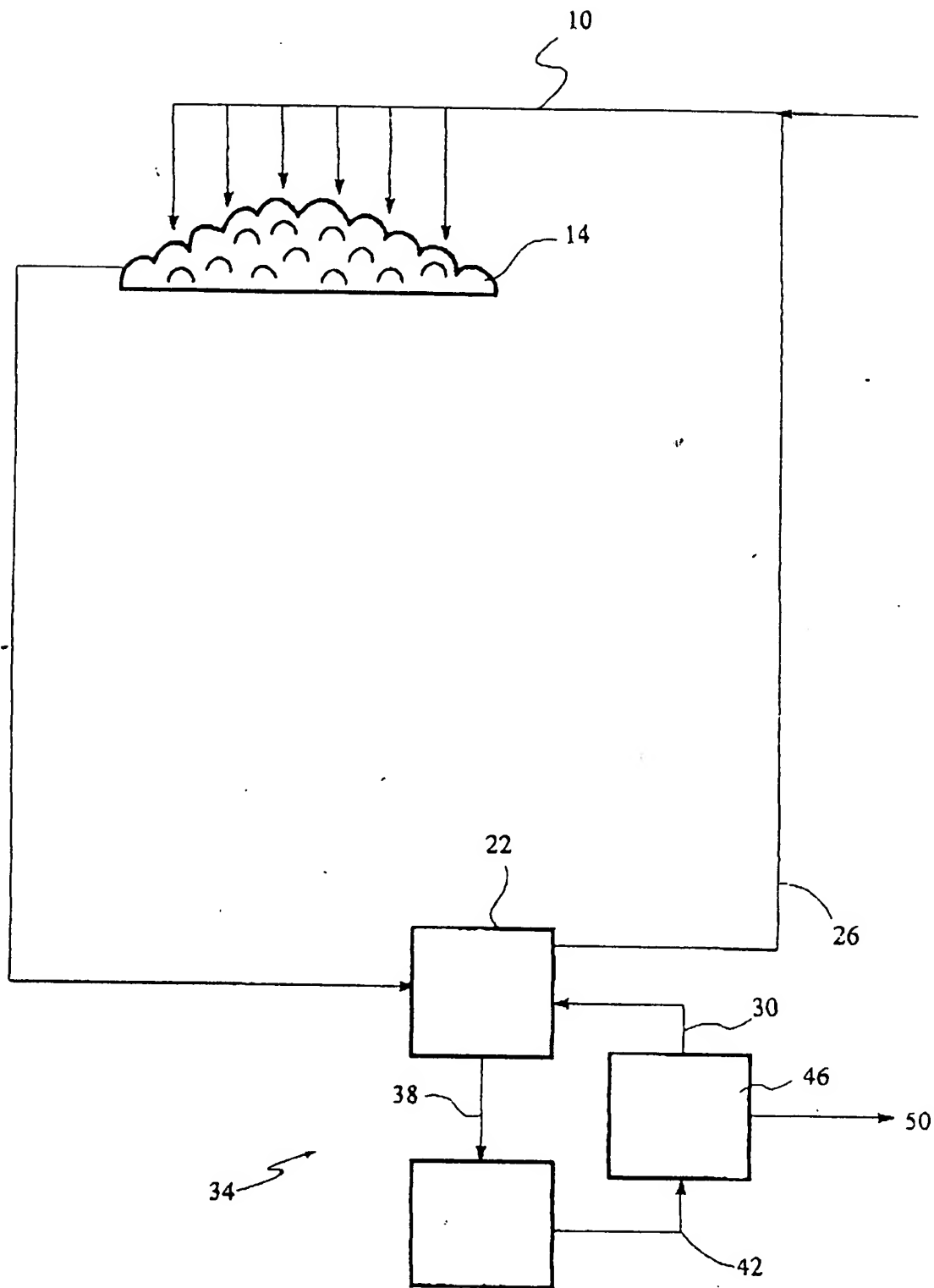


FIG. 1